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Solvent and temperature effects on the chiral aggregation of poly(alkylarylsilane)s bearing remote chiral groups.

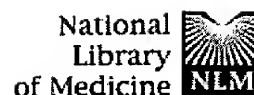
Nakashima H, Fujiki M, Koe JR, Motonaga M.

NTT (Nippon Telegraph and Telephone Corporation), Basic Research Laboratories, 3-1 Wakamiya, Morinosato, Atsugi, Kanagawa 243-0198, Japan.

Novel switchable chiroptical characteristics of poly(alkylarylsilane) microaggregates, controllable by the choice of good/poor solvent ratio (solvent polarity), solvent addition order, and sample temperature are described. The formation of stable chiral aggregates depends critically on the polysilane structure and stereochemistry. Poly[n-hexyl-(p-(S)-2-methylbutoxyphenyl)silane] (1), optically inactive in molecularly dispersed THF solution due to the existence of dynamically equivalent amounts of right (P)- and left (M)-handed screw sense helical main chain domains, shows a marked bisignate CD signal due to the formation of chiral aggregates in good/poor cosolvent systems. The sign and magnitude of the CD signals are dependent on solvent polarity, solvent addition order, and thermal effects. The less sterically hindered poly[methyl-(p-(S)-2-methylbutoxyphenyl)silane] (2) exhibits a weak, bisignate, nonswitchable CD signal in only the toluene/acetonitrile system, and no CD signals are evident in pure toluene or THF due to masking of the helicity. In contrast, although the even less sterically hindered, less polar poly[methyl-(m-(S)-2-methylbutoxyphenyl)silane] (3) does show optical activity in pure THF or toluene (negative CD signal at 310 nm), the CD signal disappears on formation of aggregates in good/poor cosolvent systems.

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Particle size analysis of concentrated phospholipid microemulsions¹. Total intensity light scattering.

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Water-in-oil phospholipid microemulsions prepared from a constant total surfactant/cosurfactant concentration of 25 wt% at four different lecithin/alcohol weight ratios (Km of 1:1, 1.5:1, 1.77:1, and 1.94:1) and containing water concentrations (or volume fractions) ranging from 2.0 to 26 wt% (or 0.04 to 0.26) have been examined at 298 K using total intensity light scattering. The data obtained were analysed using the hard-sphere model of Percus-Yevick, modified to account for the partitioning of the alcohol between the various phases. The light-scattering results showed that, regardless of the Km or the alcohol used, a minimum water concentration of at least 9 wt% was required for the formation of a microemulsion; although this value was reasonably constant for each of the investigated, there was a tendency for a slightly higher concentration of water to be required for microemulsion formation at higher Km values. Simple calculations suggested that a microemulsion was formed only when sufficient water was present to satisfy the hydration of both the phospholipid head groups and the hydroxyl groups of the cosurfactant associated with the droplet. At water concentrations lower than this minimum value, a cosolvent system was observed. In all systems above this minimum concentration, as the concentration of water increased, the size of the microemulsion droplets also increased. Surprisingly, however, there was little difference in the size of the microemulsion droplets obtained with the different alcohols, regardless of the Km, although for a particular alcohol there was some indication that the higher Km systems produced the slightly smaller droplets for an equivalent water concentration. There was also a suggestion that the more hydrophobic alcohols produced slightly smaller droplets than the more polar alcohols at the same Km.

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